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APPLICATION OF SUPERFAST ELECTRONS FOR A MICRODIFFRACTION STUDY OF THE STRUCTURE OF SOOT PARTICLES

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The method of obtaining an electron-optical image and an electron-diffraction spectrum from a very small region of one and the same object, called microdiffraction ([1]), substantially expands the possibilities of electron diffraction and electron microscopy. Modern commercial electron microscopes with an accelerating voltage of not more than 100 kV do not permit the diameter of the region of the object from which a diffraction pattern can be obtained to be reduced to a value below 1μ, owing to the insufficient brightness of the diffraction pattern.

This limitation can be overcome by increasing the velocity of the electrons, which makes it possible to increase the brightness of the image of the diffraction spectrum without increasing the thermal load on the object. With an increase in the velocity of the electrons, the permissible thickness of the object under investigation also increases, and the resolution of the diffraction pattern increases (because of a reduction in lens aberrations).

The present investigation was carried out on an electron microscope with an accelerating voltage of 400 kV ([2]) (relativistic velocity 557 keV, wavelength 0.0165 Å, resolving power in the image 20 Å), on which it was possible to reduce the diameter of the microdiffraction region to 500 Å.

In Fig. 1 the arrangement of the lenses forming the image in this instrument is shown schematically. In the upper focal plane of the objective is the object; in the lower one a movable aperture diaphragm is installed. Near the intermediate "diffraction" lens, in the plane of the image of the first stage, a movable selector diaphragm is installed. When operating "for an image," the image of the first stage is transferred by the diffraction lens into the focal plane of the projection lens, and an image of the object appears on the screen or photographic plate. By a corresponding reduction of the ampere-turns of the diffraction lens, the diffraction spectrum is transferred to the screen; its primary image is located in the lower focal plane of the objective lens. The selector diaphragm introduced into the plane of the primary image (with the aperture diaphragm removed) cuts out on the image a region of the object whose diameter is as many times

Fig. 1 schematic diagram with labels: Object; Objective lens; Aperture diaphragm; Selector diaphragm; Diffraction lens; Second image; Projection lens; Final image.

Figure 1: Fig. 1 schematic diagram with labels: Object; Objective lens; Aperture diaphragm; Selector diaphragm; Diffraction lens; Second image; Projection lens; Final image.

smaller than the diameter of the diaphragm as the magnification of the objective lens. When the diffraction lens is changed to

Fig. 1

the diffraction pattern obtained on the final screen in diffraction mode corresponds strictly to that portion of the object which was limited by the image of the selector aperture. By introducing an aperture diaphragm, any reflection of the diffraction spectrum can be isolated on the screen. On then switching to imaging, a partial dark-field image of the object is obtained, in which the bright regions correspond to favorably oriented atomic lattice planes with the indices of the reflection.

The objects of study were particles of thermal soot, both the original material and after isothermal annealing in an inert atmosphere at 3200° for 20 min. According to X-ray data, the annealed soot had a comparatively high degree of homogeneous graphitization ($\gamma = 0.78$) ([4,5]).

Figure 2a shows a bright-field image (negative) of a particle of annealed thermal soot, in which circles indicate the images of the selector aperture 600 Å in diameter, as well as the diffraction spectra (b, c, d, e, f) of the corresponding regions of the particle (indicated by arrows). The layer lines formed in the electron diffraction patterns of the individual regions are arranged along the radii of the particle. The zero layer line contains a number of bright reflections, representing reciprocal-lattice nodes of graphite with indices $00l$ (basal reflections). The character of the diffraction patterns indicates that they arise from individual crystalline blocks of the graphitized soot particle. The radial orientation of the lines of the basal reflections in the electron diffraction patterns of regions of the particle corresponds to the radial direction of the normals to the basal planes of the graphitized blocks making up the particle. In those cases where the selector aperture cuts out a region at the edges of two adjacent graphite blocks (Fig. 2f), two rows of basal reflections appear, the angle between them characterizing the mutual orientation of the blocks. This can be observed especially clearly at large angles between the directions of the basal planes of adjacent blocks. The intense arcs and rings that appear in this case indicate the presence between the blocks of an interlayer of ungraphitized carbonaceous substance. The amorphous nature of the material of these interlayers is confirmed by the absence in the electron diffraction pattern of diffraction rings with indices hkl, $h0l$, and $0kl$. The shape and dimensions of the graphitized blocks and amorphous interlayers

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

can be observed directly in the image of the particle. Each graphitized block can be distinguished especially clearly in the partial dark-field image of the particle (Fig. 2g), obtained with an electron beam of the basal reflection indicated by an arrow in Fig. 2f (the position of the image of the aperture diaphragm is shown in Fig. 2f by a circle).

The linear size of the largest blocks is ~ 1500 Å, and the mean thickness of the interlayer is 200–300 Å. In the electron diffraction patterns of the graphitized blocks, elongation of the reflections with indices 100; 101; 102; 110; 112, etc., along the equator, with the formation of layer lines, is characteristic. This indicates an imperfect azimuthal orientation of the basal planes of the graphite crystal lattice, in agreement with X-ray data ([4]). A detailed study of the azimuthal ordering and defects of the crystal lattice in the graphitized blocks is connected with further quantitative investigations of the positions, shape, and intensity of the reflections in the electron diffraction patterns.

The electron diffraction pattern of the entire particle of graphitized thermal soot, obtained with a microdiffraction-region diameter of $0.5\,\mu$, is the result of the superposition of the diffraction patterns of all graphitized blocks and amorphous interlayers. Along with diffraction rings, point basal reflections arise, whose position in the electron diffraction pattern reflects the symmetry of growth of the graphitized blocks in the soot particle during isothermal annealing.

Figure 3a shows a bright-field (negative) image of a particle of the original thermal soot and the diffraction spectra (b, c, d, e, f) of individual regions of it, 600 Å in diameter, indicated by circles. Diffraction

Fig. 2

Fig. 3

patterns are characterized by the presence of a number of basal reflections, the sharpness of which indicates a comparatively high ordering of the basal planes of carbon in the direction normal to them. In this case the layer lines formed in the electron diffraction patterns do not break up into separate point reflections (in contrast to a graphitized particle). The curvature of the layer lines, as well as a certain tangential broadening of the basal reflections, indicate a spherical orientation of the basal planes, whose normals are arranged radially. The absence of reflections with indices hkl, $h0l$, and $0kl$ attests to complete azimuthal disordering of the basal planes of carbon. The character of the electron diffraction patterns, in full agreement with X-ray data ([6]), confirms the con-

cept of the amorphous nature of the carbonaceous substance of the original soot particles. The normals of the basal planes are arranged rather strictly in the direction of the radii of the spherical soot particle, as is evidenced by the radial arrangement of series of basal reflections in the electron diffraction patterns of individual regions of the particle.

In Fig. 3 it is very clearly seen that the angular disordering of the arc-shaped reflections in the electron diffraction patterns is greater the closer the region of microdiffraction study is to the center of the spherical particle. This is natural, since as one approaches the center of the particle the curvature of the spherical carbon layers increases. In this example we see how a "spherical" texture, indeterminate by the usual method of "macrodiffraction," can be resolved into a series of oblique textures by the method of microdiffraction.

The data obtained from the study of the structure of soot particles agree with the concept of the probable mechanism of their growth ([7]), according to which aromatic synthetic products of gas pyrolysis are orientedly condensed on the surface of particles, possibly in the form of embryonic flat atomic networks of aromatic carbon with side radicals. The growth of carbon networks proceeds in the solid phase through processes of thermal destruction and synthesis in the side radicals. These processes, as may be supposed, lead to the formation of a polymeric structure of the carbonaceous substance of soot particles in the form of an aggregate of oriented aromatic carbon networks, spatially cross-linked through side radicals. The spherical form of soot particles is explained by the uniform deposition of carbonaceous substance from the gas phase over the entire surface of the particle. The atomic-molecular structure of soot particles is similar to the structure of lustrous carbon, which differs only in the symmetry of packing of the flat carbon networks ([7]). As was shown earlier ([8]), in lustrous carbon deposited on the walls of the reaction vessel, planar packing of the carbon networks is observed under the influence of the flat substrate.

Microdiffraction of electrons of increased velocities opens new possibilities for a detailed study of the atomic structure of carbon. The high penetrating power of ultrafast electrons makes it possible to obtain images and diffraction patterns from relatively large carbon particles, while the reduction of the microdiffraction region, also associated with the increase in electron velocity, makes it possible to investigate by the diffraction method not only individual particles but also their internal mosaic.

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Note: Figure translations are in progress. See original paper for figures.